Supporting information

A chiral thiourea and a phosphazene for fast and stereoselective organocatalytic ring-opening-polymerization of racemic lactide.

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1. Experimental section

Materials. *L*-LA (Corbion-Purac) and *rac*-LA (Sigma-Aldrich) were recrystallized three times from dry toluene. Afterwards, lactide was purified by azeotropic distillation. Lastly, they were dried under dynamic vacuum for overnight prior to use. (*R*, *R*) and (*S*, *S*) - Takemoto's catalyst (TUC), received from Strem Chemicals, were dried azeotropically under dry toluene 3 times. Benzyl alcohol (BnOH), received from Alfa Aesar, was purified by cryo-distillation over calcium hydride (CaH₂). Phosphazenes bases P₂-*t*-Bu (2 M in THF) and P₁-*t*-Bu, were purchased from Sigma-Aldrich and used without further purification. Benzoic acid (≥99.5%, Sigma-Aldrich) was used as received. THF was distilled over Na/benzophenone and toluene over polystyryl lithium prior to use. DCM was distilled over CaH₂ before use following a minimum of 4 h of reflux.

Instrumentation. ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ on Bruker Advance instrument at 400 MHz at room temperature. Homonuclear decoupled ¹H NMR spectroscopic measurements were recorded at room temperature on Bruker Advance instrument at 400 MHz and CDCl₃ was used as an internal reference (δ = 7.26). The relaxation time was fixed to 2 s. Samples were obtained in CDCl₃ solutions with the decoupling pulse based on the methyl region (~ δ = 1.5 ppm).

Equimolar model (1:1) experiments. One to one experiments were conducted in NMR Young tubes to ensure inert atmosphere along the whole measurement. The preliminarily flame dried NMR Young tubes, were filled inside the argon atmosphere of the glove-box. Toluene-d8 was distilled over polystyryl lithium prior to use.

Thermal annealing experiments. For this purpose, a known amount of the polymer was stirred vigorously at 200 rpm overnight close to its melting point. The as-treated sample was then removed from the oil bath and allowed to cool down to room temperature and held for 24 hours, before re-analysis by DSC.

Polymer molar masses were determined by size exclusion chromatography (SEC) using tetrahydrofuran (THF) as the eluent. Measurements in THF were performed on an Ultimate 3000 system from Thermoscientific equipped with diode array detector DAD. The system also includes a multi-angles light scattering detector MALS and differential refractive index detector dRI from Wyatt technology. Polymers were separated on three G2000, G3000 and G4000 TOSOH HXL gel columns (300 x 7.8 mm) (exclusion limits from 1000 Da to 400 000 Da) at a flowrate of 1 mL/min. Columns temperature was held at 40°C. Polystyrene was used as the standard using a correction factor of 0.58.

Positive-ion MALDI-MS experiments were conducted using a Waters QTOF Premier mass spectrometer equipped with a Nd:YAG laser (third harmonic) operating at 355 nm with a maximum output of 65 μ J delivered to the sample in 2.2 ns pulses at 50 Hz repeating rate. Time-of-flight mass analysis was performed in the refraction mode at a resolution of about 10K. All samples were analyzed using trans-2-[3-(4-tert-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as a matrix. Polymer samples were dissolved in THF. Additionally, 50 μ L of 2 mg/mL Nal solution in acetonitrile was added to the polymer solution.

 $T_{\rm g}$ and $T_{\rm m}$ values were determined by differential scanning calorimetry (DSC) using a DSC Q100 RCS TA Instrument. Polymer samples were first heated to 220 °C at 10 °C/min, equilibrated at this temperature for 10 min, then cooled to -10 °C at 10 °C/min, held for 10 min, and reheated to 220 °C at 10 °C/min. All thermal data were obtained from the first scan.

General polymerization methods.

All polymerizations were performed at room temperature: Pre-dried 10 and 50 mL Schlenks were first introduced into an Argon-filled glovebox. In a typical polymerization reaction [*rac*-LA]₀/[(Phosphazene base: TUC)]₀/[BnOH]₀= 200/(1:1)/1, Toluene (1 ml), P₁-*t*-Bu (1 equivalent, 0.01 mmol, 2.35 µL) and (S,S) Takemoto catalyst (1 equivalent, 0.01 mmol, 4 mg) were added into a dry 10 ml Schlenk flask. After 20 minutes of stirring, a solution of benzyl alcohol (BnOH) in toluene (0.4 M in toluene, 1 equivalent, 0.01 mmol, 25 µL) was added. The mixture was stirred for 10 minutes and then added into a 50 ml Schlenk containing a solution of *rac*-lactide (200 equivalents, 2 mmol, 288 mg in 24 ml of toluene). Polymerizations were performed in glovebox and monitored by ¹H NMR spectroscopy and SEC before precipitation. Polymerizations were then quenched by addition of benzoic acid. The polymer was

subsequently precipitated from cold methanol (MeOH), and after filtration it was excessively washed with methanol to remove any impurities. All polymers were dried under dynamic vacuum for overnight. Monomer conversion was calculated by comparing the integration of the methyl signals of unreacted monomer to the methyl region of the polymer before precipitation. Theoretical molar masses ($M_{n, theo}$) were calculated from ¹H NMR spectra from the monomer conversion factor (x_{LA})

Run	Catalyst (C)	[M] ₀ /[C] ₀ /[I] ₀	Time	Conv	$ar{M}n_{calcd}$	$\bar{M}n_{_{exp}}$	D^b	P _m ^e	T _m
			(min)	(%) ª	(kg/mol) ^₅	(kg/mol) ^c			(°C) ^e
1 ^f	P₂-t-Bu/TUC	200:(1/4):1	480	89	25	27	1.15	0.6	-
2 ^g	P ₂ - <i>t</i> -Bu/TUC	200:(1/4):1	480	90	26	28	1.2	0.61	-
3 ^h	P ₁ - <i>t</i> -Bu/TUC	200:(1/4):1	300	≥99	28	23	1.12	0.84	154
4 ⁱ	P ₁ - <i>t</i> -Bu/TUC	200:(1/4):1	300	≥99	28	19	1.32	0.75	140

^{a)} Monomer conversion determined by ¹H NMR in CDCl₃ using integrals of the characteristic signals. ^{b)} $M_{n,calc} = M_{LA}$ (144.13 g·mol⁻¹) × ([LA]₀/[I]₀) × conversion + M_{BnOH} (108.14 g·mol⁻¹). ^{c)} Determined by SEC in THF relative to PS standards using a correcting factor of 0.58³⁵.^{d)} Determined by homonuclear decoupled ¹H NMR. ^{e)} Determined by DSC. ^{f)} Polymerization solvent, CH₂Cl₂. ^{g)} Polymerization solvent, THF. ^{h)} Polymerization performed at 45 °C. ⁱ⁾ Polymerization performed at 80 °C.

Table S1: ROP of rac-LA using the phosphazene/(S, S) Takemoto binary organocatalytic system.

2. Polymerization mechanism



Scheme S1. Proposed mechanism for the isoselective ROP of *rac*-LA using the binary (TUC/P₂-*t*-Bu) organocatalytic system.



Scheme S2. Plausible structure of benzyl alcohol deprotonated by P₂-*t*-Bu.

3. NMR analysis



Figure S2: Stacked homodecoupling ¹H NMR spectrum of the methine region of PLA produced using P_2 -*t*-Bu/(*S*, S) TUC (**Table 1**, runs 1, 4 and 5).



Figure S3: Stacked homodecoupling ¹H NMR spectrum of the methine region of (A) PLA produced using P_2 -*t*-Bu/TUC in DCM (red curve) and (B) PLA produced using P_2 -*t*-Bu/TUC in THF (blue curve) (**Table S1**, runs 1 and 2).



Figure S3: Stacked quantitative ¹³C NMR spectra (in CDCl₃) of (A) PLA produced using P_2 -*t*-Bu/(*S*, S) TUC (1/4) (red curve) and (B) PLA produced using P_1 -*t*-Bu/(*S*, S) TUC (1/4) (blue curve).



Figure S4: Stacked homodecoupling ¹H NMR spectrum of the methine region of (A) PLA produced using P₁-*t*-Bu/TUC at 45 °C (red curve) and (B) PLA produced using P₁-*t*-Bu/TUC at 80 °C (blue curve) (**Table S1**, runs 3 and 4).



Figure S5: Stacked ¹H-NMR experiments performed in dry toluene-d8 at room temperature with Takemoto's catalyst, P₂-*t*-Bu and P₁-*t*-Bu.

4. Polymerization kinetics



Figure S6: Plots of M_n (circle, black) and M_w/M_n (triangle, red) for PLA synthesis using P₂-t-Bu/TUC (1/4) (**Table 1**, run 5).



Figure S7: Kinetic plots of the ROP of *rac*-LA, catalyzed by (*S*, *S*)-TUC paired with P_1 -*t*-Bu at room temperature with [*rac*-LA]/ [(*S*, *S*)-TUC/ [P_1 -*t*-Bu] = 200/4/1.

5. DSC analysis



Figure S8: DSC thermograms (1st scan; 10 °C/min) of PLAs samples produced using P_2 -t-Bu/(S, S) TUC (**Table 1**, runs 1, 4 and 5).



Figure S9: DSC thermograms (1st scan; 10 °C/min) of PLAs samples produced using P₂-t-Bu/TUC (1/4) in different solvents (**Table 1**, run 5, **Table S1** runs 1 and 2).